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STABLE ISOTOPE DILUTION FOR HAZARDOUS WASTE INCINERATION

by

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ABSTRACT

This research project was undertaken with the general objective of evaluating the potential utility of isotope dilution GC/MS in chemical analysis related to incineration of hazardous waste materials. The specific objective was to determine whether a proposed catalytic exchange procedure could be adapted to produce the labeled analog materials necessary for isotope dilution GC/MS anlaysis.

The proposed deuterium exchange technique is described along with experiments designed to test its applicability. Results of those experiments show that the technique can be successfully applied to certain limited classes of hazardous waste materials, but they do not indicate sufficient versatility to meet the most general needs of hazardous waste incineration programs.

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SECTION 1

INTRODUCTION

Incineration as a means for disposing of hazardous wastes is a technology likely to see simultaneous application and development in the immediate future. Both to monitor application and to evaluate development, chemical analysis of influent streams, effluent streams and fugitive emissions is of value, and one of the appropriate analytical techniques is combined gas chromatography/mass spectrometry (GC/MS).

In the interest of obtaining the highest possible quality GC/MS data, it would be desirable to apply isotope dilution GC/MS techniques similar to those used in analysis of priority pollutants in water. The present study is intended to assess the applicability of isotope dilution GC/MS techniques to the analytical needs of incineration technology, including accurate measurement of destruction removal efficiency (DRE), identification of products of incomplete combustion (PICs), and monitoring of fugitive emissions.

The needs of incineration technology are likely to include analysis of compounds for which suitable isotopically labeled analogs are not commercially available. The present study, therefore, concentrates on experimental evaluation of a catalytic isotope exchange technique which shows considerable potential for production of deuterium labeled compounds and compound mixtures. A variation of the proposed exchange technique has been demonstrated (1) to cause a general tritium incorporation into complex organic mixtures, so it can be considered as a potential source of labeled materials in a more general sense than just a source of specific labeled compounds. As such, it promises to find a number of uses in application to the hazardous wastes which will be presented for incineration. Labeling of a complex incineration influent mixture, or a characteristic portion of it, might be feasible, allowing the analyst to spike with a realistic analog material for isotope dilution DRE estimation, or even to follow the transformations of labeled materials in PIC studies.

SECTION 2

CONCLUSIONS

Catalytic exchange is not a simple, general technique which can be used to generate deuterium labeled analogs of hazardous wastes. It is, however, a technique which could prove valuable in application to more limited classes of materials. The technique shows a surprising capability to produce labeled analogs thoroughly, extensively and specifically for several phenols, polynuclear aromatic hydrocarbons, and some other species.

For the compounds which are deuterated, the product materials are suitable for use as isotope dilution GC/MS standards or as spiking materials for process characterization.

Based on the data generated in this study for a selected set of compounds, the major limitation of the technique seems to be its lack of generality. For the majority of compounds and compound classes represented in the test mixture, no useful labeled analogs were isolated from the reaction vial.

SECTION 3

RECOMMENDATIONS

The present study has demonstrated that catalytic exchange can be successfully applied in specific cases, but without further development it is not applicable to waste materials in general. The unsuccessful applications deserve further study to determine whether simple methodology revisions can resolve the problem. Time of exposure to catalyst and selection of extraction solvents are simple, potentially useful variations of techniques which might very well extend the list of suitable compound classes.

The present study has addressed the labeled analog problem only in very general terms, and has indicated some potentially fruitful applications of catalytic exchange in the area of hazardous waste analysis. Further work should focus on explicit needs of specific programs, with emphasis on optimizing experimental techniques for a specified, limited set of materials. PCB incineration efficiency, phenol containing wastewater cleanup or fugitive emissions of organic species from synfuel processes might be appropriate choices for areas of further study.

SECTION 4

BACKGROUND

ISOTOPE DILUTION

Isotope dilution GC/MS is a quantitative technique in which the sample is spiked with a known amount of a labeled analog of the target compound, usually labeled by incorporation of one or more ^{13}C or ^{2}H (D) atoms. Labeled and natural material pass through the sample work-up with equal efficiency, are eluted at nearly the same retention time, and are not subject to relative distortion by analyzer discrimination effects. The natural compound concentration is determined by the ratio of natural compound GC/MS response to labeled compound response (2).

It has been demonstrated that isotope dilution techniques result in superior precision, both in the long term (3) and in the short term (4, 5), and in superior accuracy (6) when compared with conventional GC/MS analysis. Furthermore, the additional cost of obtaining labeled compounds is not excessive, and the technique has been adopted for use in several effluent water monitoring projects of the EPA Effluent Guidelines Division.

A prerequisite for isotope dilution analysis is the availability of labeled analogs to the target compounds of interest. Labeled analogs are commercially available for approximately one half of the priority pollutant compounds as listed in Reference (7). These are produced by careful synthesis and purification to give 99 percent purity of specific isomers. To extend the list of available analogs to more thoroughly encompass the materials of interest in incineration studies, a simpler, less expensive means than custom synthesis is needed.

In its usual application, quantitation by isotope dilution depends on the assumption that GC/MS instrument response is proportional to concentration of injected sample, both for natural compound and for labeled analogue:

$R_N = K_N C_N$ for natural compound, and

$R_L = K_L C_L$ for labeled compound.

Where R is instrument response, C is concentration and K is the proportionality constant.

The ratio of R_N to R_L is the isotope response ratio, R_m, as employed in EPA Method 1625.

$$R_m = \frac{R_N}{R_L} = K\ C_N$$

Where

$$K = \frac{K_N}{K_L C_L}$$

If concentration of labeled material is constant throughout calibration and analysis stages, K can be determined empirically so that only the response ratio of natural-to-labeled material is needed to determine sample concentration of natural material.

It is significant that all chemical and instrumental parameters are included in one empirically determined constant. This means it is not necessary to know either absolute concentration or purity of labeled analog, and the requirements placed on the labeled analog by the isotope dilution applications are not so stringent that highly purified specific isomers are required. The labeled analog need only be chemically indistinguishable from the natural compound and have distinguishing mass spectral features. For example, perdeuterophenanthrene, $C_{14}D_{10}$, is used as an analog for isotope dilution determination of phenanthrene. Any of the less substituted phenanthrenes, e.g., $C_{14}H_2D_8$, $C_{14}H_5D_5$, etc., would serve equally well and even simple mixtures of several isomers would do. It is only necessary that a reasonably intense mass spectral peak exist which is correlated with the amount of analog material present.

CATALYTIC EXCHANGE

The principle of replacing a hydrogen atom in an organic molecule by tritium (T) to generate a radioactive tracer molecule is a common practice in several areas of biochemical research. Several catalytic exchange reactions have been employed and studied for the purpose of optimizing yield of radiolabeled compounds (8-15), but only limited work has been done to elucidate the details of reaction mechanisms and of product structures (16-19).

A promising procedure for the production of isotopically labeled compounds from their natural analogs is the catalytic exchange reaction described by Farrier, et al., (1). That work demonstrated that the catalytic exchange conditions could be applied to complex mixtures of organic compounds, namely to those which can be extracted from oil shale retort process waters. The conclusion that a general tritiation of the

mixture, i.e., one which was not compound-specific, had occurred was implied by the equivalence of gas chromatograph analyses of product and reactant materials using flame ionization and radiochemical detection, respectively. Although no detailed chemical characterization of reactants and products was undertaken by Farrier, et al., shale oil components are known to be similar to many of the priority pollutant compounds and to form a class of materials which might one day be candidate for destruction by incineration.

Inspection of the technical literature reveals that many of the Group VIII transition metals, including nickel, are used as catalysts for hydrogenation of unsaturated organic compounds, and many have also been used to promote hydrogen exchange (8) for the purpose of labeling organic compounds with radioactive tritium. Those catalysts can be effective under mild conditions of atmospheric pressure and near-ambient temperature. The metal catalysts are known to promote side reactions such as rearrangements, decomposition and hydrogenation of some organic compounds (9,10,11), but side reactions are less severe when the heavy isotope is introduced as HTO rather than as HT. Compounds containing sulfur, iodine or nitrate groups do not readily undergo exhange (9,12).

Adam's catalyst (PtO_2) and platinum black (13) have been used quite extensively as catalysts in the deuterium exchange reactions of organic compounds. The simpler aromatics, such as benzene, pyridine and phenol, exhibited a greater percentage of exchange than did polynuclear aromatics, such as chrysene and phenanthrene (9,12). The ability of aliphatic compounds to undergo deuterium exchange is generally lower and less complete than that for aromatic compounds (12). Table 1, from Reference 9, illustrates these tendencies.

Also evident from this table is the limited exchange of sulfur and nitrogen-containing compounds. Adam's catalyst was used with D_2O at 130°C for these exchange studies. Table 2 from Reference 16 provides similar information about effectiveness of Raney nickel catalyst.

Deuterium exchange utilizing the platinum catalyst in an acidic medium has also been done (10,11,14,17). The results of these studies are similar to the non-aqueous platinum-catalyzed exchange reactions. Cholesterol, for example, shows an atom percent exchange that varies from 0.07 percent to 5.7 percent, depending upon reaction conditions (11). Also, under certain conditions cholesterol decomposes to hydrocarbons and steroid ketones (6,11).

Hydrogenation occurs as a side reaction during the deuterium exchange reaction (16,17). In the study of toluene, up to 10 percent of the starting material was found to be converted to methylcyclohexane (16). The amount of hydrogenation that occurs can be controlled by the reaction

TABLE 1. (from Ref. 9)
EFFECTIVENESS OF PtO_2 CATALYZED HYDROGEN
EXCHANGE FOR SELECTED COMPOUNDS

Compound	Atom Percent Exchange	Reaction Time (hr)
Benzene	50	45
Phenol	44	71
Pyridine	35	48
Chrysene	8.7	48
Phenanthrene	8.7	48
Anthracene	2.9	48
Cyclohexane	0.4	48
Dibenzyl	28	48
Naphthalene	2.5	48
n-Octane	2.0	48
Nitrobenzene	0.1	3.5
Thiophene	1.3	45
Anisole	15.4	71
Pyrrole	45	45

TABLE 2. (from Ref. 16)
HYDROGEN EXCHANGE EFFICIENCIES FOR ALKYL AROMATIC HYDROCARBONS USING RANEY NICKEL CATALYST

Compound	D Content*	Aromatic	Aliphatic
Toluene	1.776	0.603	1.173
Ethylbenzene	1.770	0.657	1.113
Isopropylbenzene	1.608	0.900	0.708
t-Butylbenzene	1.225	1.225	0.000
Mesitylene	1.674	0.006	1.668
o-Xylene	1.765	0.180	1.585
m-Xylene	1.770	0.075	1.695
p-Xylene	1.720	0.036	1.684

*Deuterium atoms per molecule.

conditions or by how the Raney nickel catalyst is prepared. However, reaction conditions which optimize the deuterium exchange can also increase deuterium addition side reactions.

SECTION 5

EXPERIMENTAL PROCEDURES

The overall experimental strategy in this study was to carry out an initial catalytic exchange experiment chosen on the basis of the background information presented in the preceeding section. The Raney nickel procedure of Farrier, et al. (1), was selected for initial evaluation. A second set of experiments was then carried out using an improved experimental technique and employing PtO_2 as the catalyst. The two sets are discussed separately in this section.

A set of 27 test compounds was chosen to represent various classes of compounds on the list of candidate principal organic hazardous constituents (POHCs) (19) associated with hazardous waste incineration. A mixture of these representative POHCs was prepared and characterized by GC/MS using fused silica capillary columns. The results of this standard mixture analysis were used as reference mass spectra of natural compounds, as retention time reference points, for relative abundance precision determination and for quantitative calibration.

The test compound mixture was then subjected to the Raney nickel exchange procedure as described in this section. At the conclusion of that first set of experiments, several problem compounds were identified, so a new POHC mixture was prepared for the second exchange procedure. Several compounds were deleted because they had proven unsatisfactory for the analytical scheme, and the relative concentrations were increased for some compounds for which poor recovery from the reaction vial had been observed. The second mixture was then subjected to the PtO_2 procedure.

In addition, a PCB mixture, Aroclor 1254, was prepared, analyzed, and subjected to the isotope exchange procedure. Since Aroclor 1254 is itself a mixture of 40 or 50 major and minor components, it was treated separately from the POHC mixture.

The first exchange procedure is an adaptation of the heterogeneous catalysis technique from Reference 1. Ten mg of each organic compound were added to 300 mg of Raney nickel catalyst activated by the technique of Dominiguez, et. al. (19), and 2.0 mL of D_2O which is the deuterium source. The reaction vial was sealed and heated in an oil bath maintained at 105°C +5°C. The reaction was allowed to proceed for six days with magnetic stirring to mix the contents before the reaction vial was removed from the oil bath.

As soon as the reaction mixture had cooled to room temperature, the liquid (D_2O) was decanted off and extracted five times with 2.0 mL

methylene chloride. The combined extract was concentrated under a stream of dry N_2 to 3.5 mL and spiked with 2,2'-difluorobiphenyl internal standard for GC/MS analysis. The Raney nickel slurry was transferred to filter paper and washed three times with 2 mL of methylene chloride. The methylene chloride wash was concentrated to 2.7 mL before spiking with internal standard and analysis by GC/MS. For the initial PCB experiment, only the water extract was obtained and analyzed. Analytical conditions were as specified in EPA Method 625, except that a fused silica capillary column was used in the GC/MS instrument to enhance sensitivity and chromatographic resolution.

As discussed in Section 6 of this report, the results of the Raney nickel catalyzed exchange reactions were inconclusive, and several potential improvements were suggested. These considerations led to a second set of experiments, including control experiments to determine the extent to which deuteration can occur without catalyst. For the latter purpose, a reaction vial was prepared with deuterated solvent and the test compounds only, heated to 110°C with stirring for six days, extracted and analyzed as was done for the PtO_2 procedure.

The second set of catalytic exchange experiments was carried out with platinum (IV) oxide. The PtO_2 is added to a 4:1 mixture of D_2O/CD_3OD and purged with D_2 gas for four or five minutes at room temperature. The catalyst changes from black to chocolate brown as it is transformed into its active form. The activated catalyst/solvent slurry is purged with N_2 to minimize the undesirable catalytic deuterium addition side reaction which is favored in the presence of D_2 gas. One milliliter of test compound solution (1 to 3 mg of each compound in methylene chloride) is then added to a vial containing 700-mg active catalyst and 4 mL of D_2O/CD_3OD mixture. The vial is capped and heated to 110°C with stirring for ten days. Extraction and analysis are as described for the Raney nickel experiments, except that the extracts of the two phases are combined prior to analysis.

SECTION 6

RESULTS AND DISCUSSION

The experiments discussed here are intended to evaluate the utility of catalytic hydrogen isotope exchange reactions in producing deuterium labeled materials for isotope dilution GC/MS analytical techniques. In order to present the data in a form which is appropriate to that purpose, data are presented in units related to the isotope response ratio, R_m, as defined in section 4 of this report. To a first approximation, R_m is directly proportional to the ratio of natural material to labeled material, and its inverse, R_D, is proportional to the labeled:natural ratio. In the present context, R_D is a measure of the success of the catalytic exchange in transforming natural material into its labeled analog.

R_D is defined as:

$$R_D = \frac{A_L}{A_N}$$

Where A_L is the area under the extracted ion current profile (EICP) at the characteristic mass of the labeled compound and A_N is the EICP area at the characteristic mass of the natural compound.

The POHC deuteration results are presented in Tables 3 (Raney nickel catalyst) and 4 (PtO_2 catalyst). For comparison purposes, Table 3 includes R_D values measured in the uncatalyzed control experiment, mean R_D's measured from a triplicate analysis of standard reference compounds, and "true" R_D's calculated from the natural abundance of ^{13}C in the POHC's. Each table is accompanied by an explanatory narrative containing definitions and comments.

TABLE 3. POHC/RANEY NICKEL RESULTS

	Test Compound	R_D	Percent Deuterated	Control R_D	Observed Natural R_D	True Natural R_D
1.	phenol	0.351	22	0.168	0.055	0.067
2.	2,4-dimethylphenol	0.444	29	0.169	0.074	0.089
3.	2-chlorophenol	0.477	29	0.151	0.061	0.067
4.	2,4-dichlorophenol	0.290	17	0.074	0.056	0.067
5.	2,4,6-trichlorophenol	(a)	-	-	-	-
6.	p-chloro-m-cresol	(a)	-	-	-	-
7.	2,4-dinitrophenol	(b)	-	-	-	-
8.	4,6-dinitro-o-cresol	(b)	-	-	-	-
9.	benzidine	(b)	-	-	-	-
10.	2,4-dinitrotoluene	(b)	-	-	-	-
11.	2,6-dinitrotoluene	(b)	-	-	-	-
12.	nitrobenzene	(b)	-	-	-	-
13.	pyridine	0.084	3	0.030	0.047	0.056
14.	p-nitroaniline	0.074	0	0.111	0.055	0.067
15.	toluene diisocyanate	(b)	-	-	-	-
16.	N-nitrosodi-n-propylamine	0.063	0	0.061	0.063	0.057
17.	4-bromophenylphenylether	0.127	0	0.116	0.122	0.133
18.	bis (2-chloroisopropyl) ether	(a)	-	-	-	-
19.	1,4-naphthoquinone	(b)	-	-	-	-
20.	phthalic anhydride	(b)	-	-	-	-
21.	dimethylphthalate	0.096	0	0.085	0.079	0.111
22.	1,2,4,5-tetrachlorobenzene	(a)	-	-	-	-
23.	fluoranthene	0.180	0	0.163	0.173	0.178
24.	chrysene	0.202	0	0.185	0.194	0.200
25.	benzo(a)pyrene	0.223	0	0.188	0.209	0.222
26.	aldrin	(a)	-	-	-	-
27.	lindane	(b)	-	-	-	-

EXPLANATION OF TABLE 3

The first column contains data from GC/MS analysis of Raney nickel catalyzed reaction product, while columns 3,4 and 5 are from the uncatalyzed control experiment, triplicate standard analysis and theory, respectively. See the explanation of Table 6 for more detail. Column 2 contains the translation of the R_D values into a more familar form: percent of product molecules containing a single deuterium. There is no evidence for significant multiple deuterium incorporation and all R_D are derived with m/z characterisic of single substitution.

(a) Means an interference precluded reliable response measurement.

(b) Means the compound was not recovered from the reaction.

TABLE 4. POHC/PtO_2 RESULTS

	Test Compound	Product R_D	Standard R_D	M_L	M_H	No. D
1.	phenol	(b) >1000	0	99	94	5
2.	2,4-dimethylphenol	(c) 37.6	0	127	122	5
3.	2-chlorophenol	(a)	-	-	-	-
4.	2,4-dichlorophenol	(d) 1000	0	164	162	2
5.	2,4,6-trichlorophenol	(a)	-	-	-	-
6.	p-chloro-m-cresol	(a)	-	-	-	-
7.	2,4-dinitrophenol	(a)	-	-	-	-
8.	4,6-dinitro-o-cresol	(a)	-	-	-	-
9.	benzidine	(a)	-	-	-	-
10.	2,4-dinitrotoluene	(a)	-	-	-	-
11.	2,6-dinitrotoluene	(a)	-	-	-	-
12.	nitrobenzene	(a)	-	-	-	-
13.	pyridine	(a)	-	-	-	-
14.	p-nitroaniline	(a)	-	-	-	-
15.	toluene diisocyanate	(a)	-	-	-	-
16.	N-nitrosodi-n-propylamine	(a)	-	-	-	-
17.	4-bromophenylphenylether	(a)	-	-	-	-
18.	bis (2-chloroisopropyl) ether	(a)	-	-	-	-
19.	1,4-naphthoquinone	(a)	-	-	-	-
20.	phthalic anhydride	(e) 17.2	0.002	106	104	2
21.	dimethylphthalate	(f) 173	0	168	163	5
22.	1,2,4,5-tetrachlorobenzene	0.113	(g)	215	214	1
23.	fluoranthene	(h) 352	0	212	202	10
24.	chrysene	53.4	0	236	228	8
25.	benzo(a)pyrene	(i) >1000	0	262	252	10
26.	aldrin	(j)	-	-	-	-
27.	lindane	(a)	-	-	-	-

EXPLANATION OF TABLE 4

Data in column No. 1 are measured from GC/MS analysis of the product recovered from the experiment, and column No. 2 values are from the triplicate analysis of the standard POHC mixture. M_L and M_N are the characteristic masses for labeled product and unlabeled reactant, and the degree of deuterium exchange corresponding to the chosen M_L is in the last column.

(a) No labeled or unlabeled product was recovered.

(b) Substitution at the hydroxyl site is reversed during analysis. Product is 100 percent D_5-phenol.

(c) Product is a mixture of D_4-, D_5- and D_6-dimethylphenol, and the spectra indicate more ring substitution than methyl substitution.

(d) Product is 100 percent D_2-dichlorophenol which implies that a specific one of the 3 possible sites is not active toward catalytic exchange.

(e) Phthalic anhydride hydrolyzes rapidly on contact with water, so it is surprising to detect any of it at all. The product is 90 percent D_2-phthalic anhydride. Several additional products were detected which could not be positively identified, but which appear to be structurally related to phthalic anhydride and also appear to be deuterated.

(f) Product is predominantly D_8-dimethylphthalate with small amounts of D_9- and D_{10}-analogs. In all cases, the methyl groups are entirely deuterated and at least 2 aromatic sites are substituted.

(g) See Table 6.

(h) Product is about 75 percent D_{10}-fluoranthene with D_9- and D_{11}-analogs making up the remainder.

(i) Product is 100 percent D_{10}-benzo(a)pyrene, which leaves two unsubstituted sites.

(j) Deuterium labeled aldrin was detected, but the extent of substitution could not be determined and no characteristic m/z could be identified for isotope dilution use.

Table 5 contains PCB data from both catalytic systems and Table 6 summarizes QA/QC data for the POHC's.

TABLE 5. PCB RESULTS

Peak No.	Characteristic Masses	Number Chlorine	Raney Nickel Experiments		PtO_2 Experiments		
			Product R_D	Reactant R_D	Product R_D	Reactant R_D	Control R_D
1	223/222	2	N*	N	0.14	0.06	0.11
2	"	2	1.6	0.12	0.17	0.13	0.07
3	257/256	3	0.47	0.10	N	N	N
4	"	3	0.39	0.10	N	N	N
5	"	3	0.15	0.12	0.12	0.06	0.03
6	"	3	0.54	0.14	0.13	0.13	0.10
7	"	3	0.22	0.90	0.18	0.09	0.15
8	291/290	4	0.15	0.11	0.06	0.03	0.08
9	"	4	0.20	0.11	N	0.07	0.12
10	"	4	0.51	0.06	0.08	0.05	N
11	"	4	0.18	0.07	0.08	0.04	0.06
12	"	4	0.38	0.08	0.06	N	0.06
13	"	4	0.14	0.11	0.05	0.08	0.08
14	"	4	N	N	0.03	0.07	0.06
15	"	4	N	N	0.09	0.06	0.06
16	325/324	5	0.16	0.07	0.09	0.05	N
17	"	5	0.12	0.10	0.10	0.04	0.10
18	"	5	0.16	0.09	0.04	0.04	0.05
19	"	5	0.14	0.06	0.08	0.03	N
20	"	5	0.18	0.07	0.02	0.03	N
21	"	5	0.14	0.08	0.01	N	0.07
22	"	5	0.15	0.10	0.05	N	0.09
23	"	5	N	N	0.31	0.19	0.26
24	359/358	6	0.12	0.09	0.09	N	N
25	"	6	0.12	0.10	0.07	0.03	N

*N means response too low for meaningful measurement.

The two Raney nickel experiments gave different results. There was considerable deuterium incorporation into the PCB's, but disappointingly little into the other test compounds. Control experiments were run with both samples under conditions identical to the PtO_2 experiments, but without catalyst. As expected, the controls showed no deuteration of PCB's and slight deuteration of some POHC's. The POHC's affected are essentially those deuterated in the Raney nickel test, but they are substituted to a lesser extent. The compounds are largely phenols which could be expected to exchange their acid hydrogens with D_2O, then undergo a slow intramolecular exchange.

The PCB results indicate that Raney nickel catalytic exchange can be successful. The failure of Raney nickel to deuterate the test mixture satisfactorily is attributed to shortcomings of the particular experiment. Two suspected problems are catalyst deactivation by test compounds or by excess atmospheric oxygen, and inadequate contact between catalyst and compounds. The latter problem is related to the low solubilities of some test compounds in water and exaggerated by a mechanical malfunction of the magnetic stirring apparatus.

Rather than undertake a more detailed study of the Raney nickel system, a second catalytic system was chosen for evaluation, and the insights into experimental difficulties provided by the Raney nickel work were applied to experimental design for the second system. Platinum (IV) oxide was chosen as the second catalyst because it is known to be a more effective hydrogen exchange catalyst than Raney nickel. PtO_2 requires more carefully controlled experimental conditions and is more likely to promote side reactions, but it has the advantage that its active form can be visually distinguished from the poisoned form. Care was taken to avoid the potential problems of the Raney nickel experiment by excluding air during catalyst preparation and by allowing contact only with deuterated solvents. With the intent of improving contact between target compounds and catalyst, the solvent system was modified to be a CH_3OD/D_2O mixture in which the compounds should be more soluble than in pure D_2O.

The most optimistic interpretation of Farrier's earlier experiments, i.e. that exchange of hydrogens could be implemented in a manner that was not compound specific, has not been confirmed. The primary reason is apparently strong interaction between target compounds and catalyst such that a large number of target compounds are not recovered by normal solvent extraction. In the Raney nickel experiment, where the catalyst effectiveness was apparently compromised, only 17 of 27 (63 percent) target compounds were recovered, and from the more active PtO_2 system, only 10 of 25 (40 percent) were recovered. This, coupled with the "no catalyst" control experiment where 21 of 25 (84 percent) were recovered, implies that catalyst systems which effectively promote hydrogen exchange are also active at driving other processes which result in loss of compound.

Whether these processes are destructive chemical reactions or merely strong adsorption phenomena is not known, but might possibly be determined by further experimentation.

On the other hand, the generality of deuteration for those compounds which were recovered is high. Nine of the 10 compounds recovered from the PtO_2 system had undergone substantial deuteration. If additional compounds can be extracted from the catalytic reaction system by different solvents and revised procedures, there is good reason to expect that they too will be deuterium labeled.

With the exception of aldrin, the products of the PtO_2 exchange reaction are also deuterated in such a way that useful labeling has been achieved. The large R_D numbers demonstrate that deuterium incorporation has produced analogs with little or no interference between labeled and natural mass spectra. In general, a large fraction of the hydrogen atoms have been replaced with deuterium, and several compounds have been converted almost entirely to one specific isomer. Aldrin produces a complex mass spectrum that is poorly suited to GC/MS quantitation in any case and the mass spectrum of its labeled analog is not suitable for isotope dilution quantitation. In the course of the first experiments, it was discovered that toluene diisocyanate reacts so rapidly with the small amounts of water in methylene chloride as to proclude its analysis even in the standard mixture. Consequently, it was not included in the PtO_2 experiment. Phthalic anhydride simply disappeared from the first experiment, but was recovered, along with several unidentified but deuterated products from the PtO_2 run. This is a surprising result which requires further study in order to explain the reaction mechanism.

The same three experiments - Raney Nickel catalyzed exchange, PtO_2 catalyzed exchange and a catalyst free control run - were applied to PCB reactant with mixed results. The test material selected was Aroclor 1254, a common PCB mixture which contains predominantly biphenyls substituted with 3, 4, 5 and 6 chlorines. Analysis data from the Raney nickel experiment show that very good R_D measurements can be obtained under conditions which are conventional for GC/MS analysis of environmental samples. Furthermore, PCB recoveries from the reaction vial are straightforward so that the characteristic chromatogram is preserved through the deuteration treatment.

Significant PCB deuteration is observed following Raney nickel treatment. While the extent of deuterium incorporation is not large - only about one PCB molecule in five has gained a deuterium atom - even the small observed R_D values are sufficient to make this a useful labeled Aroclor for some kinds of tracer studies. The Raney nickel results are also grounds for optimism that a catalytic exchange technique can be developed to satisfactorily label PCB mixtures.

The encouraging Raney nickel results for Aroclor 1254 are in conflict with discouraging data from the PtO_2 equipment. As discussed in Section 7, the GC/MS data are themselves inconclusive. It is clear, however, that the improved deuteration efficiency of PtO_2, which was demonstrated for the POHC test mixture, was not realized for the PCBs.

In a more limited context than general labeling of uncharacterized mixtures, the exchange experiments do indicate potential usefulness. There are classes of compounds, phenols, polynuclear aromatic hydrocarbons, and perhaps PCB's, which can be extensively and easily deuterated.

When these classes are representative of a waste material to be incinerated, catalytic exchange can be used to prepare labeled analog material which is suitable for isotope dilution GC/MS application. Catalytic exchange could also be used in such cases to prepare labeled spiking materials for use in process characterization.

SECTION 7

QA/QC SUMMARY

The overall goal of the present reseach project is to evaluate a proposed, but very poorly characterized technique for the production of labeled materials to be used in isotope dilution GC/MS analysis. A decision was made to commit available resources toward the broadest possible survey of the proposed technique at the expense of detailed study of narrower facets of that proposal. For this reason, few data were generated to help assess the overall reproducibility of the total exchange experiment by such means as replicate experiments.

The paucity of overall QA/QC data leaves the QA burden on the analytical techniques which were used to evaluate the general experiments, most heavily on the GC/MS instrumental analysis and the associated sample preparation and data analysis. These techniques must be relied upon to characterize the experimental results accurately, precisely and completely.

EPA Method 1625 is the standard isotope dilution quantitative GC/MS method, so the majority of QA/QC procedures employed were identical to those described in Method 1625. This includes preparation of reagents and calibration standards, DFTPP abundance pattern tuning criteria, use of internal standard and analysis of a standard mixture before each day of sample analysis. Samples were not analyzed until tuning criteria were met and standard compound responses and chromatographic retention times had been demonstrated to be satisfactory based on S-CUBED long-term control charts.

The key parameter in the present study is a ratio of peak areas from extracted ion current profiles. It is critical that peak area measurements be accurate and precise. Both accuracy and precision were tested by a triplicate analysis of the test mixture.

Results of the triplicate analysis are presented in Table 6. The mean R_D reported is the peak area ratio which would be employed in the case of single deuterium incorporation. The "true" R_D is the ratio to be expected in the absence of any deuterium incorporation and is an accuracy standard for the measured mean R_D in this analysis.

Similar accuracy and precision information is derived from the PCB standard analysis data given in Table 5. The mean single deuterium R_D for all 21 selected peaks is 0.094 with standard deviation of 0.021. The "true" value for any unlabeled PCB is 0.111.

TABLE 6. POHC QUALITY CONTROL SUMMARY

	Test Compound	Control R_D	True Natural R_D	Mean Observed Natural R_D	Observed Standard Deviation	M_L	M_N
1.	phenol	0.168	0.067	0.055	0.005	95	94
2.	2,4-dimethylphenol	0.169	0.089	0.074	0.004	123	122
3.	2-chlorophenol	0.151	0.067	0.061	0.002	129	128
4.	2,4-dichlorophenol	0.074	0.067	0.066	0.004	163	162
5.	2,4,6-trichlorophenol	0.026	0.067	0.069	0.005	197	196
6.	p-chloro-m-cresol	(a)	-	-	-	-	-
7.	2,4-dinitrophenol	(a)	-	-	-	-	-
8.	4,6-dinitro-o-cresol	0.109	0.078	0.050	0.014	199	198
9.	benzidine	(b)	-	-	-	-	-
10.	2,4-dinitrotoluene	(c) 0.154	0.078	0.091	0.001	166	165
11.	2,6-dinitrotoluene	(c) 0.084	0.078	0.092	0.003	166	165
12.	nitrobenzene	0.057	0.067	0.063	0.002	124	123
13.	pyridine	0.030	0.056	0.047	0.003	80	79
14.	p-nitroaniline	0.111	0.067	0.055	0.009	139	138
15.	toluene diisocyanate	(b)	-	-	-	-	-
16.	N-nitrosodi-n-propylamine	0.061	0.067	0.063	0.006	131	130
17.	4-bromophenylphenylether	0.116	0.133	0.122	0.002	251	250
18.	bis (2-chloroisopropyl) ether	(c) (b)	0.056	0.046	0.004	122	121
19.	1,4-naphthoquinone	(d)	0.111	0.103	0.004	159	158
20.	phthalic anhydride	(c) (d)	0.078	0.064	0.009	149	148
21.	dimethylphthalate	0.085	0.111	0.079	0.009	195	194
22.	1,2,4,5-tetrachlorobenzene	(a)	0.067	0.057	0.002	215	214
23.	fluoranthene	0.163	0.178	0.173	0.004	203	202
24.	chrysene	0.185	0.200	0.194	0.001	229	228
25.	benzo(a)pyrene	0.188	0.222	0.209	0.003	253	252
26.	aldrin	(e)	-	-	-	-	-
27.	lindane	(e)	-	-	-	-	-

EXPLANATION OF TABLE 6

Data in the first column are measured from the catalyst-free control experiment, and the second column data are the theoretical values for the case of no exchange. The third and fourth columns list the mean R_D values and standard deviations, respectively, measured from triplicate analysis of unreacted test mixture. M_L and M_N are the characteristic m/z chosen to make R_D reflect incorporation of a single atom of deuterium per molecule.

(a) Means interference precludes measurement.

(b) Means compound was not included in the test mixture.

(c) Means that M_L and M_N refer to fragment ions, not parent ions.

(d) Means compound not recovered from the reaction.

(e) Means the mass spectrum is not suitable for interpretation.

The accuracy and precision indicated in Table 6 and in the Raney nickel portion of Table 5 are entirely satisfactory, in fact, remarkably good for the equipment and the instrumental parameters employed in this work. The difficulty of adapting conventional GC/MS quality control measures to unique research projects is evident from the PtO_2 portion of Table 5. The mean observed R_D was only 0.062, nearly a factor of two different from the true value, with a standard deviation of 0.044. Both the low mean R_D and the large relative standard deviation result from mass spectrometer and data system thresholds being set to suppress baseline noise and other low level signals. This condition which discriminates against relatively small peaks prevails in spite of careful instrument tuning to meet Method 1625 abundance pattern specifications.

For the purposes of this study, the PtO_2 PCB data are still adequate to support the presented conclusions, but it is evident that revised instrument tuning criteria will be needed for future work of this kind.

REFERENCES

(1) "Catalytic Titration and ^{3}H NMR Spectroscopy of Complex Organic Mixtures - Applications to Oil Shale Process Waters," D. S. Farrier, J. R. Jones, J. P. Bloxsidge, L. Carrol, J. A. Elridge and M. Saieed, Journal of Labeled Compounds and Radiopharmaceuticals - Vol. XIX, p. 213 (1981).

(2) B.N. Colby, Final Report, EPA Contract No. 68-02-3153.

(3) "Strategies for Compound Identification and Quantification Using Fused Silica Capillary Column CG/MS," B. N. Colby, P. W. Ryan, and J. E. Wilkinson, HRC and CC, in press, 1983.

(4) A. D. Sauter, L. D. Betowski, B. N. Colby, J. E. Wilkinson, and T. R. Smith, presented at the 1981 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., March 1981.

(5) A. D. Sauter, L. D. Betowski, T. R. Smith, V. A. Strickler, R. G. Beimer, B. N. Colby, and J. E. Wilkinson, HRC and CC 4, (1981) 366.

(6) A. D. Sauter, P. E. Mills, W. L. Fitch and R. Dyer, HRC and CC 5 (1982) 27.

(7) Federal Register, Vol. 44, No. 233, Dec. 3, 1979, pp. 69532-69552, Methods 624 and 625.

(8) "Isotopic Hydrogen Labeling of Heterocyclic Compounds by One-Step Methods," G. E. Calf and J. L. Garnett, in Adv. in Heterocyclic Chemistry, Vol. 15, p. 137 (1973).

(9) J. H. Garnett, W. A. Sollich, Australian J. Chem. 15, 56 (1962).

(10) D. K. Fukushima, T. F. Gallagher, J. Biol. Chem. 198, 861 (1952).

(11) K. Bloch, D. Rittenberg, J. Biol Chem. 149, 505 (1943).

(12) J. H. Garnett, Nucleonics 20, 86 (1962).

(13) L. C. Leitch, Can. J. Chem. 32, 813 (1954).

(14) M. L. Edinoff, J. E. Knoll, S. Ann. Chem. Sec. 75, 1992 (1953).

(15) H. S. Anker, K. Bloch, J. Ann. Chem. Soc. 66, 1752 (1944).

(16) L. Horner, D. Mayer, B. Michael, H. Hoenders, Liebigs Ann. Chem. 679, 1 (1964).

(17) L. Horner, J. Grohmann, Liebigs Ann. Chem. 670, 1 (1963).

(18) L. Horner, D. Mayer, Liebigs Ann. Chem. 680, 1 (1964).

(19) Federal Register, Vol. 45, No. 98, May 19, 1980, Appendix VII, p. 33132.

(20) X. A. Dominguez, I. C. Lopez, and R. Franco, J. Org. Chem. 26, p. 1625 (1961).